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Trace metals on the Algarve coast, I: Associations, origins and remobilisation of natural components

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ABSTRACT

The deep red colours observed on the topmost portions of cliffs along the Algarve coast are due to the presence of goethite/haematite pigments dispersed within the predominantly sandy sediments. Chemical and mineralogical analyses of these iron-enriched Pliocene/Quaternary siliciclastic sediments and of samples of terra rosa taken from carstic cavities in neighbouring calcareous terrains indicate the genetic link between these materials on the Algarve coast. The authors suggest that the terra rosas which developed on Tertiary and Mesozoic limestones were transported and deposited on top of sandy sediments cropping in a coastal area of the Algarve, during the period of erosion in Late Pliocene/Early Quaternary times. The distribution of trace elements in these sediments supports the conclusion that the later process of remobilisation and redistribution of the ferruginous pigments led to the formation of hardpans, globules and crusts. The dissolution and reprecipitation of the iron oxides leads to the transformation of goethite into haematite.

Key words: Iron oxides, trace elements, leaching, adsorption.

RESUMEN

Metales traza en la franja costera del Algarve, I: asociaciones, orígenes y remobilización del componente natural

Los colores rojo oscuro encontrados en las camadas superiores de los acantilados a lo largo de la costa del Algarve se deben a la presencia de pigmentos de goetita/hematita dispersos en los sedimentos predominantemente arenosos. Los análisis químicos y mineralógicos de muestras de estos sedimentos siliciclásticos enriquecidos de hierro, pertenecientes al Plioceno/Cuaternario, así como de las muestras de terra rosa *tomadas de las cavidades cársticas en los terrenos calcáreos circundantes, permiten establecer la conexión genética entre ellas en la franja costera del Algarve. Se postula que, durante el periodo de erosión, las* terra rosa *desarrolladas sobre las calizas de Terciario y Mesozoico fueron transportadas y depositadas encima de los sedimentos arenosos aflorantes en el área costera del Algarve. El análisis de la distribución de elementos trazos en estos sedimentos ha permitido concluir que el último proceso de remobilización y redistribución de los pigmentos ferruginosos condujo a la formación de* hardpans*, glóbulos y costras. La disolución y reprecipitación de los óxidos de hierro, condujo a la transformación de la goetita en hematita.*

Palabras clave: *Óxidos de hierro, elementos trazos, lixiviación, adsorción.*

INTRODUCTION

The detrital Pleistocene (probably including part of the Pliocene) deposits of the Algarve are separated from underlying Middle to Upper Miocene (Boski *et al.,* 1995; Moura and Boski, 1997) calcarenites by a prominent discontinuity (unconformity) marked by an extensive carstification surface. The lithological profile at Santa Eulalia, which was the principal sampling site for the present study (figure 1), may be considered very typical for the entire region.

These sediments belong to the prograding deltaic/alluvial fan series whose lateral extension exceeds 150 km along the southern Atlantic coast of the Algarve and Andalusia. Gambelas sand and gravel is the upper member of this sedimentary sequence defined as the Ludo formation by Moura and Boski (1994), and which is characterised by an intense iron oxide/hydroxide pigmentation. Given the high porosity and permeability of the entire Ludo formation, iron and accompanying elements undergo continuous leaching, enhanced by vegetation, and may be precipitated into the lower portion of sedimentary sequence or exported in solution directly to marine sediments and water. They therefore contribute to the higher geochemical background values found by Machado *et al.* (in this volume) in the organic tissues of marine organisms. The processes of accelerated cliff erosion (Correia *et al.*, 1996) and seasonal rainfall erosion are responsible for producing the suspension loading of ferruginous pigments into the coastal waters. The present paper reports on the first phase of a regional study aimed at elucidating the origins of these ferruginous pigments and their pathways during remobilisation, together with associated heavy-metal traces.

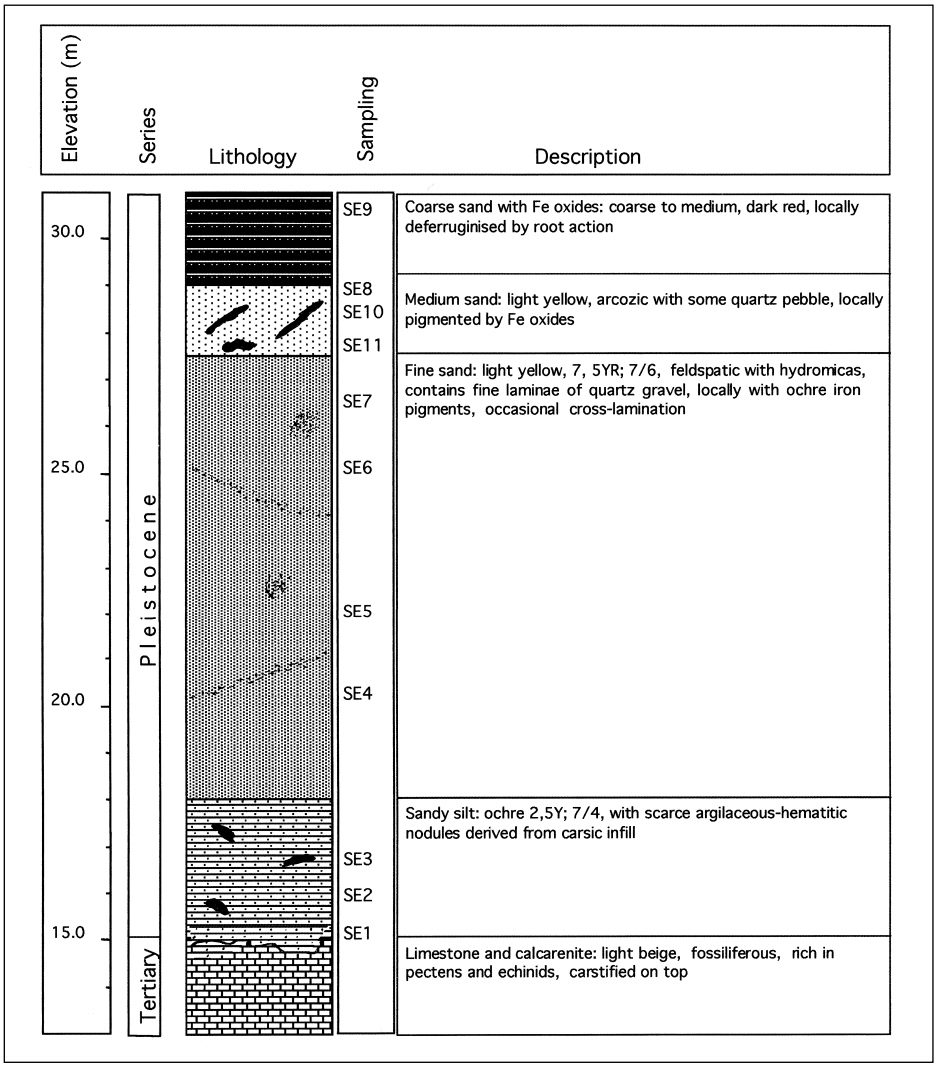

Figure 1. Lithological profile of Neogene-Quaternary sediments at Santa Eulalia (central Algarve)

MATERIALS AND METHODS

The following sediment samples, all from Portugal except for the second, were collected for analysis:

– 11 (SE) from a complete Plio-Pleistocene profile at Santa Eulalia (figure 1)
– 3 (BON) from the topmost part of ferruginised sediments in Bonares (Spain)
– 2 (BAR) from surface ferruginous crusts on Praia de Barranco
– 2 (TR) of terra rosas from carstic cavities in Loulé and Boliqueime
– 2 (OA) of Fe- and Mn-enriched sediments in Olhos de Água
– 1 (GO) from the sediment profile at Galé.

The map in Machado *et al.* (in this volume) shows the localisation of sampling sites in the Algarve. All samples were ground integrally in an agate planetary mill down to the fraction > 200 mesh and prior to chemical analyses, were dissolved in HCl after alkaline fusion, or were solubilised directly through hot triacid digestion.

Chemical analyses

Alkaline fusion was applied in order to allow us the determination of subsequent of major elements, i.e. Fe, Ti and Mn. Approximately 0.5 g of powdered sample was thoroughly mixed with 3.7 g of Norish flux (lithium tetraborate + lithium carbonate + lanthanum oxide), placed in a platinum crucible and fused at 1 100 °C during 10 min in the electric muffle furnace. The melt was dissolved in 1:8 nitric acid of analytical purity and made up to the final volume of 500 ml.

Acid dissolution was applied to the aliquots of sediment prepared like the above samples in order to conduct further analyses of trace elements. Approximately 0.5 g of each sample was submitted to triacid digestion (20 ml HF, 10 ml HNO_3, 2 ml $HclO_4$) followed by dissolution in water and making the volume up to 500 ml. The elemental concentrations were determined by inductively coupled plasma atomic emission simultaneous spectrometry (apparatus ARL3500C). The analytical accuracy was checked every 6 determinations by running international standard BXN.

Mineralogical analyses

The non-oriented powder aggregates were placed in aluminium holders by gently pressing powdered samples against filter paper. X-ray diffractograms were obtained from a Siemens D5000 apparatus equipped with graphite monochromator and a Cu anticathode lamp maintained at 45-kV and 35-mA current. The analytical slit was set at 0.03° and the goniometer speed at 0.5°/min. XRD peaks were identified by means of a DIFFRAC-AT program and the Al-substitution in goethite was estimated from the 010-line shift (Shulze, 1984) persistent in solution

DISCUSSION

Both terra rosa samples reveal almost identical mineralogies, which were dominated by kaolinite, goethite, quartz and muscovite. The sample SE3, from the base of Santa Eulalia profile, presented a similar mineralogical composition and colour. This suggests that it must have originated from carstification of the surface of the Miocene biodetrital calcarenite. In all the remaining samples, the identified minerals were plagioclases (in the lower part of the Santa Eulalia profile), microcline, kaolinite and muscovite. Goethite was the only iron mineral identified, although the deep red colour (10YR3/2) of samples SE3 SE9 and SE10 and the terra rosas lead us to assume, according to Boero and Schwertmann (1987), the presence of a small percentage of haematite. The remaining iron-rich samples, like those of globules and crusts, have much more ochre tints; therefore, the presence of haematite in these samples must be ruled out. From this observation, the preferential leaching of haematite due to the greater thermodynamic stability of goethite can be deduced, in particular when the latter mineral is Al substituted (Tardy and Nahon, 1985). The analysed diffractograms show the goethite d111 peaks at approximately 2.452 Å systematically displaced in the direction of higher 2Q angles. This enabled Fitzpatrick and Schwertmann (1982) to estimate the Al-for-Fe substitution rate in the SE3, SE9 and both terra rosa samples at 14% (molar). Manganese oxides were not detected directly from raw sample diffractograms. However, complementary sampling in the immediate vicinity of sample OA28 (Olhos de Água

cliff, 28 m asl) of a larger volume of sediment, and elimination of quartz grains from this material, revealed the presence of todorokite in the new diffractogram.

Chemical composition in terms of the 10 elements analysed is shown in table I. Given the relatively small number of samples, the statistical treatment of these data was limited to the analyses of simple bivariate correlations and regression.

The sediment profile studied at Santa Eulália was enriched in iron oxides on its uppermost and lowermost portions. In the lower part, the ferro-argilaceous nodules observed within the sandy sediment (samples SE1 SE2 and SE3) are, beyond any doubt, derived from the underlying carstified surface, which must undergo some erosion prior to the deposition of the siliciclastic ediments. In fact, these three samples project within the terra rosa trend defined by the Fe/Ti regression line in figure 2B and also visible on the Fe/Mn scattergram (figure 3).

These three elements were chosen as referenced from the 10 analysed because of the marked differences in terms of their mobility in a hypergene environment, i.e. Ti being the most immobile, Fe intermediate and Mn the most persistent in solution (Kabata Pendias and Pendias, 1984).

The middle portion of the profile was occupied by sandy sediment with occasional coarser (gravelly) levels. The Fe content of these samples was low, as was the content of other analysed transition metals, all of them falling within the terra rosa

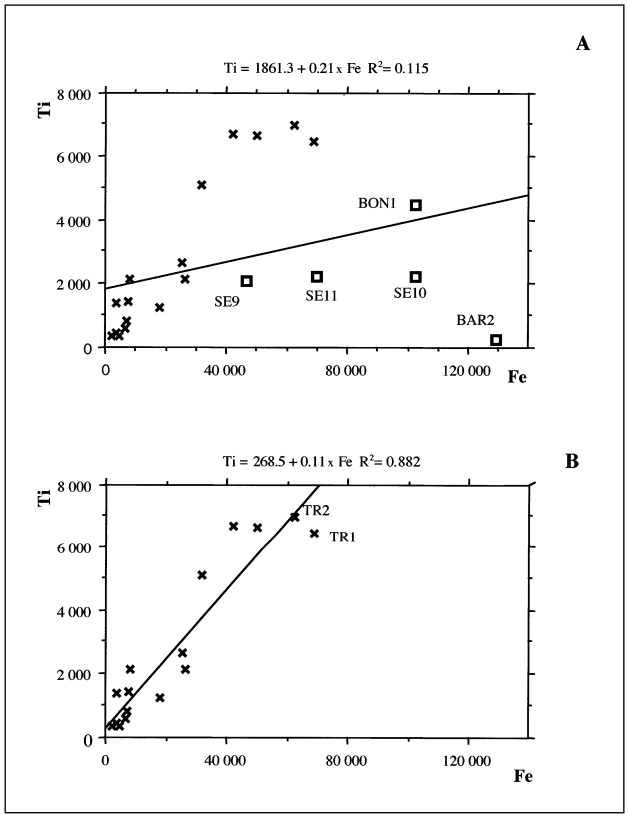

Figure 2. Ti/Fe [ppm] bivariate correlation/regression diagram. (A): All 21 analysed samples considered. (B): 5 iron-enriched samples excluded

Table I. Major and trace element contents (ppm) in terra rosas and Quaternary sediments from the Central Algarve and Andalusian littoral

Sample	Fe	Mn	Ti	Ni	Cr	Cu	Zn	Pb	Ba	V
3GO	7 770	51	1 420	22	25	9	26	40	266	20
SE1	18 170	109	1 220	30	27	3	20	23	174	26
SE2	32 390	445	5 100	56	77	25	55	54	220	96
SE3	42 720	742	6 670	70	94	34	72	64	246	120
SE4	2 450	nd	341	16	17	nd	7	46	313	3
SE5	4 930	nd	330	16	18	nd	7	53	294	7
SE6	4 180	nd	424	26	18	nd	15	41	252	8
SE7	6 960	nd	565	14	21	nd	13	26	158	11
SE8	8 250	nd	2 120	24	51	2	8	30	62	43
SE9	46 930	16	2 070	25	56	8	20	47	61	65
SE10	102 080	273	2 270	23	91	10	26	59	43	190
SE11	71 510	57	2 290	22	71	9	24	60	50	93
BAR1	25 670	93	2 640	36	57	17	44	41	146	70
BAR2	132 380	625	154	117	45	66	117	51	215	240
BON1	101 920	268	4 490	32	100	18	43	71	54	204
BON4	26 730	27	2 110	23	50	7	19	34	34	66
BON6	3 920	26	1 345	20	26	5	32	16	26	14
OA24	50 240	1 560	6 620	580	224	51	126	77	370	156
OA28	7 510	16 790	785	1 786	333	26	53	17	1 775	6
TR1	63 010	910	6 980	96	129	41	80	118	221	203
TR2	69 078	1 056	6 451	102	107	50	73	92	245	189

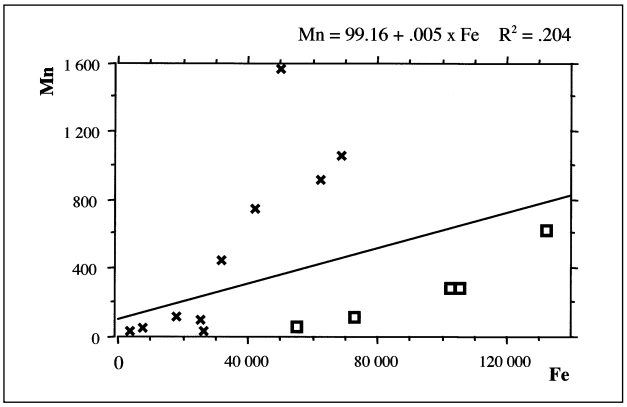

Figure 3. Mn/Fe [ppm] bivariate correlation/regression diagram. Sample 0A28 not plotted

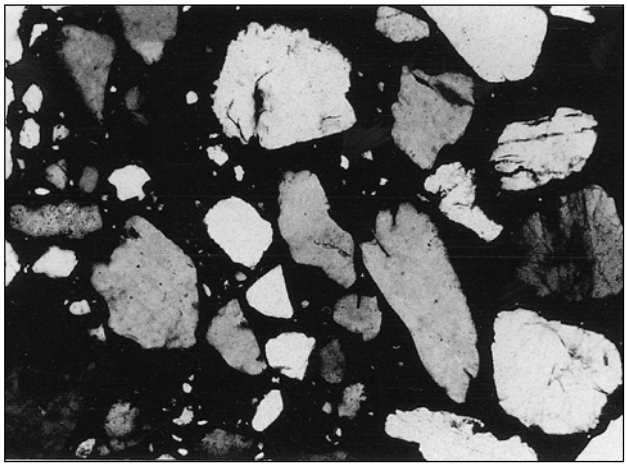

Figure 4. Microphotograph of iron crust (crossed nicols) showing corrosive contact between surfaces of quartz grains and ferruginous cement

trend. This suggests a conservative (essentially physical) dispersion of ferruginous pigments within silicilastic particles, without the involvement of chemical process. Barium content is inversely related to Fe content which, in our opinion, reflects marine influence (Church, 1979; Deahairs, Stroobants and Goeyens, 1991) during the deposition of this sedimentary sequence. The special affinity of Ba to Mn oxides, pointed out by numerous authors (e.g. Burns and Mee Burns, 1979), is well expressed by sample OA 28, which has the highest Mn content as well as the highest Ba content.

Sample 0A 28 could not actually be plotted on figure 3 because its high Mn content would require changing the scale from linear to logarithmic.

The three uppermost samples from Santa Eulalia profile, as well as the samples BAR2 and BON1, fall within the area of absolute Fe enrichment on the bivariate Ti/Fe regression diagram (figure 2A) and represent cases of a local addition of iron oxides via precipitation from circulating solutions. The textural characteristics of these samples confirm this finding; hence, figure 4 shows a microphotography of the most Fe-enriched sample (BAR2-crust fragment) on which the corrosive contact between quartz grains and ferruginous cement is very clear, and the multiphase Fe migration process accompanied by dissolution of silica (Nahon, 1976) is also striking. The formations of similar iron-enriched tubular structures was reported at Roupar Basin, Spain by Barral Sila and Gitian Ojea (1991), which may be explained by confined flow conditions or fingering (Hillel and Baker, 1988). It must be stressed that iron leaching and consequent import to the coastal environment is an ongoing process, as may be judged, for example, from fresh ochre precipitates on the surfaces of the cliffs at Olhos de Água. In the same locality, a direct precipitation of iron (ferrihydrite) in seawater was observed at the sites of underwater discharge of a coastal semiconfined aquifer (Vale, pers. comm.). Manganese concentration shows a trend to decrease overall in parallel to Fe enrichment. This is explained by comparatively more sluggish attainment of insoluble tetravalent form by the Mn ion (Postma, 1985) after leaching from the parent material (terra rosa). The highest enrichment in Mn was found in two samples from Olhos de Água (OA24 and OA28), probably due to the longer percolation pathway of the solutions, which enabled separation of this element from Fe. Both samples presented the highest concentrations of all the analysed metallic trace elements, due to the known affinity of cations to negatively charged manganese colloidal oxy/hydroxides (Traina and Donner, 1985; Boski and Herbosch, 1990).

The present state of iron oxy/hydroxide dispersion within the sediments of the Ludo formation, as well as their transfer to the marine environment, together with accompanying metallic trace elements, could be explained as resulting from the following sequence of processes (figure 5):

(A): Erosion of terra rosa from carstic traps during the Pleistocene emergence of calcareous Barrocal massif and the deposition of ferruginous pigments, together with sandy and gravely deposits of the Ludo formation. Dry climatic conditions were prevailing during this period.

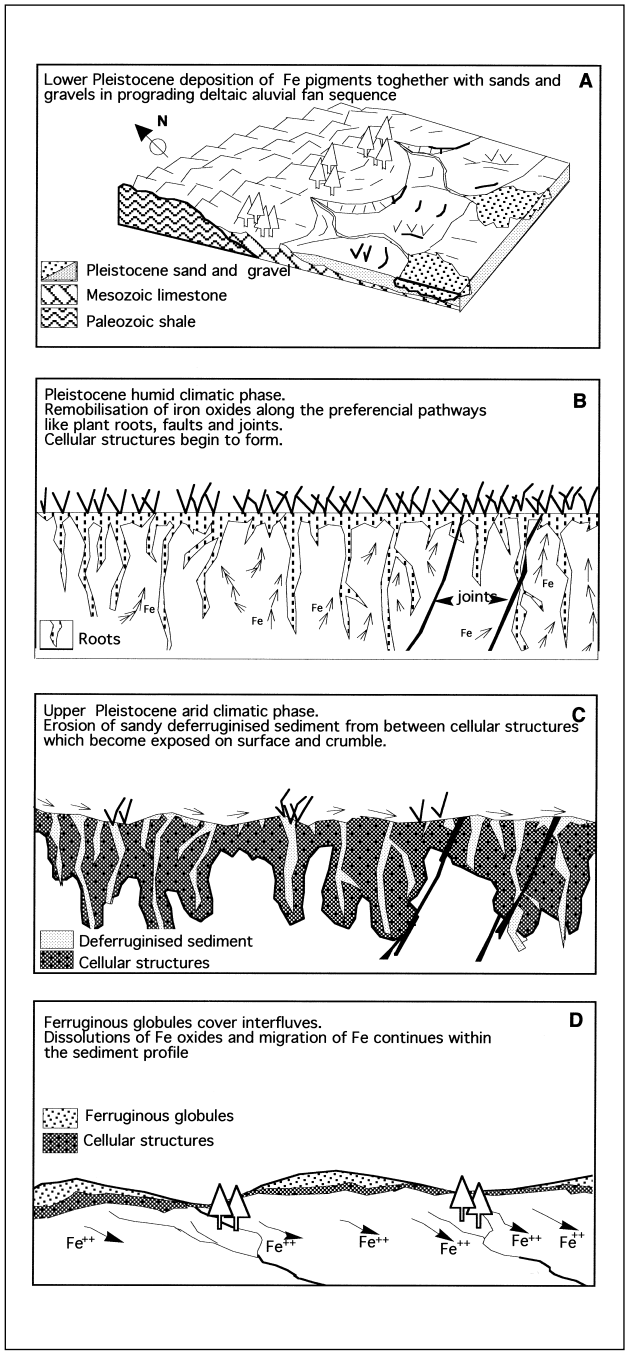

Figure 5. Four stages of formation of ferruginous crusts and globules through dissolution and reprecipitation of iron and accompanying metallic trace elements within Quaternary sediments of central Algarve and Andalusian littoral

(B): Beginning of the remobilisation of the Fe oxy/hydroxides that migrate within the sandy sediments. Plant roots, joints, fault planes and stratification surfaces act as preferential pathways for migration of these solutions and contribute to the formation of cellular structures. Humid climatic conditions prevailed during this period.

(C): In a dryer Upper Pleistocene phase, the sandy sediment was eroded from the deferruginised parts of cellular structures, leaving a skeletal structure which crumbles and covers the sediment surface with a loose mantle of ferruginous globules.

(D): The ferruginous globules were spread by colluvial process on the surface of interfluves. Iron, Mn and other metallic trace elements are exported from within the sandy sediments to marine waters, in solution or as a result of cliff erosion.

It must be considered that all of these processes may not occur sequentially, but may very well act in parallel, controlled by a set of environmental factors, e.g. local climate, sea level and tectonic activity.

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